Investigations of Electronic Minority Charge Carrier Conductivity in La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{2.85}

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Abstract. The perovskite structured material LaGaO₃ doped with 10 mol-% strontium and 20 mol-% magnesium was prepared by two different wet-chemical synthesis routes. The total conductivity was measured in air and under an oxygen partial pressure of 10⁻²⁰ bar. There was a decrease by 10 % in 4 days when the atmosphere was changed from air to 10⁻²⁰ bar. This process is reversible. Hebb-Wagner measurements resulted in values for the electronic minority charge carrier conductivities in pure oxygen of log σₜ [S/cm] = -4.02 and log σₑ [S/cm] = -15.5 for the holes and electrons, respectively, at 600 °C. In the partial pressure range 10⁻¹ bar < p(O₂) < 1 bar, a slope of +1/4 was observed for d(log (σₑ))/d(log (p(O₂))) at T = 600, 650 and 700 °C. That is in agreement with the assumption of a large number of oxygen vacancies. The diffusion coefficient of the holes was evaluated from the relaxation curves to be 1.1*10⁻⁷ cm²/s at 600 °C. Degradation effects were observed under highly reducing conditions which are attributed to the formation of gallium-platinum alloys and the loss of gallium oxide if O₂ is available in the gas phase.

1. Introduction

Presently, a major environmental problem is the greenhouse effect due to the exhaust gases from combustion processes of hydrocarbons. Several approaches are pursued to reduce the amount of these gases. One strategy is the exact control of the fuel to air ratio in automobiles by using the lambda probe in combination with a catalyst. Yttria stabilized zirconia (YSZ) is being employed as electrolyte with sufficiently high and almost pure oxide ion conduction at temperatures above about 600 °C. Another approach is the replacement of internal combustion engines by solid oxide fuel cells (SOFC). Again, YSZ is being taken into consideration as oxide ion conductor. The high operating temperature of YSZ raises many problems. For instance, very expensive interconnector materials are required for operating temperatures at around 1000 °C when individual cells are combined to stacks.

Much work was performed during the last decades to develop new electrolytes with a conductivity at temperatures around 800 °C which is comparable to that of YSZ at 1000 °C. Such a compound with high ionic conductivity is gadolinium doped ceria (CGO) which has also a fluorite structure; but this material shows predominant n-type electronic conduction in reducing atmospheres [1]. Another group of materials has the perovskite structure. This structure has the flexibility to substitute the cations by dopants with quite different ionic radii. This opens a wide field of varying the electrical properties of the material.

The history of perovskites with high oxide ion motion dates back to 1971 when Takahashi and Iwahara reported oxide ion conductivity in LaAlO₃[2]. In the early 1990's, Ishihara replaced aluminium by gallium and started substitution of the A- and B-cations by lower valent cations to form O₂⁻ vacancies. In the course of these investigations, La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{2.85} (LSGM) turned out to be the most promising candidate to substitute YSZ as electrolyte in view of the high ionic conductivity of 0.1 S/cm at 800 °C [3]. This was confirmed by other groups [4,5]. Doubts about the practical application came up with regard to the stability. Feng et al. [5] investigated a single
fuel cell for 140 h which showed no change in the performance, and Ishihara et al. reported investigations on LSGM in reducing atmospheres for 3000 min with negligible degradation [6]. In contradiction with these results, Yamaji reported gallium depletion from the surface in the case of reducing atmospheres [7]. The reasons for this observation could be the increased gallium activity which results in the formation of gallium-platinum alloys and the evaporation of gallium oxides.

In this work we investigated the total conductivity of LSGM in various atmospheres. The Hebb-Wagner technique [8,9] was employed to measure the electronic minority charge carrier contribution to the total conductivity.

2. Experimental Aspects

2.1. Powder Preparation. Wet-chemical preparation routes were chosen for the preparation of LSGM because a homogeneous mixture of the various chemical elements on an atomic level is required to exclude the formation of additional phases as reported by [10]. One technique was the sol-gel process [11] and the other one the so-called Pechini method [12]. For the sol-gel process, lanthanum acetate (99.9%, Chempur), strontium acetate (99%, Chempur), magnesium acetate (99.5%, Fluka) and gallium nitrate (6% in H2O, Chempur) were dissolved in 200 ml dest. water. After dissolution, 50 ml ammonium hydroxide (30%) were added for peptization and the solution reached a pH of 10. The solution was heated to evaporate the water and ammonium acetate. The obtained gel was calcined at 600 °C for 3 h and sintered at 1400 °C for 12 h in air. The product was grinded and pelletized by isostatic pressing at 4200 bar. A final sintering process was carried out at 1400 °C for 12 h.

The other preparation technique started with the dissolution of citric acid in ethylene glycol. An aqueous solution of lanthanum nitrate (99.99%, Chempur), strontium nitrate (99.9%, Chempur), magnesium nitrate (99.9%, Chempur) and gallium nitrate (6% in H2O) was added and a chelate complex was formed. Heating of this solution up to 100 °C forms the polymer which was decomposed by further increasing the temperature to 750 °C for 2 h. The resulting powder was pressed isostatically into bars and sintered at 1450 °C for 6 h in air. The bodies prepared according to both preparation paths were cut into pellets of 1 mm in thickness and 8 mm in diameter. The presence of a single perovskite phase was confirmed by powder X-ray diffraction using a Seiffert (XRD 3000) diffractometer (Fig. 1).

2.2. Conductivity Measurements. Two-probe ac-impedance spectroscopy was employed to measure the conductivity of the samples. Platinum paste was painted onto both sides of the pellets and then heated up to 850 °C for 1 h. The measurements were carried out using an HP 4192A impedance analyzer with a frequency range from 5 Hz to 13 MHz and an amplitude of 50 mV. The reducing atmospheres were produced by mixtures of CO and CO2.

2.3. Hebb-Wagner Measurements. The principle of the method is the blocking of the ionic current by using an inert sealed negative electrode and a reversible positive electrode with a fixed oxygen partial pressure. The resulting current is therefore provided by electrons and holes only. In order to keep the diffusion controlled equilibration time short, the measurements were made initially by using electrolytes of only 100 μm in thickness [12]. Later we used samples of 1 mm in thickness. A schematic view of the cell used for the present investigations is shown in Fig. 2. Platinum paste was again painted onto both sides of the electrolyte. Then, a glass ring was placed on top of